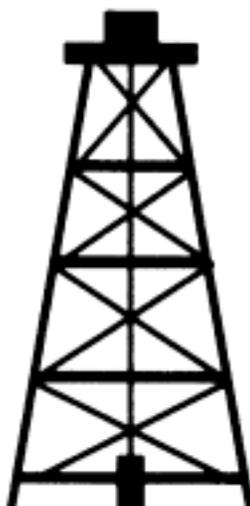


SOUR HYDROCARBONS - THE ELASTOMER CHALLENGE'

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INTRODUCTION

Hydrofluorocarbon elastomers, ASTM designation D1418-FKM, are produced domestically by Dupont and 3M Company under the trade names of Viton and Fluorel. FKM elastomers have been extensively studied, and ample published information is available both from suppliers and from journals such as Rubber Chemistry and Technology (RC&T). This paper deals primarily with interactions resulting from increasing weight-per cent of fluorine and increasing molecular weight of FKM elastomers in the "sour" hydrocarbon environment, not previously reported. With a few exceptions, most of the data utilized are available from RC&T and the Rubber Division's book "Science and Technology of Rubber."

EXPERIMENTAL

Early work on FKM formulations had indicated high molecular weight polymers (FKM1C) had superior mechanical properties in gas-liquid refrigeration applications. Initial testing in the sour crude environment confirmed this observation. We believed increasing weight-per cent fluorine elastomers would show further improvements, a fallacious assumption.

Backbone cleavage was presumed and subsequently proven as another incorrect assumption¹. This led to a more rigorous evaluation of molecular weight relationships and physical modulus characteristics, key properties of the original FKM seal compounds.

DISCUSSION AND RESULTS

Elastomers-The Panorama

Mechanical properties.-"The strength and extensibility of an elastomer depend on its overall viscoelastic properties." This is part of Smith's introductory statement in his paper, "Strength of Elastomers-A Perspective."² Table I from this work neatly defines the elastomer we are studying. Strength and toughness are desired physical characteristics, one created by molecular mobility and the other by molecular immobility, a two phase condition, not available in hydrofluorocarbon (FKM) elastomers. FKM elastomers are categorized according to Smith as: filled, single-phase, non-crystalline materials.

Physical state and temperature.-Figure 1³ is an idealized plot of shear modulus versus temperature. This curve represents all single phase, non-crystalline, filled or unfilled, crosslinked elastomers. The highest shear value represents the fracture energy of a typical crystalline material. The 1000 fold decrease in shear modulus with increasing temperature is a typical characteristic of this category of elastomers. Logically, increasing molecular weight increases the melt temperature, and crosslinking extends the rubbery plateau.

Figure 2, modulus (Young's modulus E) vs. temperature is a plot of real world FKM1 data⁴ representing the circled area in Figure 1. Shear modulus is 1/3 to 1/4 Young's modulus (dependent on filler loading). This transition zone should be avoided in dynamic applications.

The dramatic degree of change in shear modulus versus temperature points out the viscoelastic nature of elastomers. A more comprehensive background is furnished by reviewing the failure envelope concept:

Failure envelope concept.-Smith^{5,6}, in some landmark work, developed his concept of ultimate properties, a major contribution. Earlier, William's, Landel, and Ferry, with their WLF equation, pointed out that all polymers, regardless of their chemical structure, will exhibit similar viscoelastic behavior at equal temperature intervals (T-Tg) above their respective glass-transition temperatures. Smith has added to this concept by showing that the ultimate tensile properties of a non-reinforced, amorphous, crosslinked elastomer can be characterized by a failure envelope which is independent of time (strain rate) and temperature.

Figure 3 from Reference 5 schematically illustrates the general effect of strain rate and temperature on the tensile, stress-strain properties of amorphous elastomers. The lines originating from 0 represent stress-strain curves determined at various strain rates and temperatures. The envelope ABC connects the rupture points. The rupture point moves counter clockwise around the "failure envelope" as either the strain rate is increased or the test temperature is decreased.

OA represents classical stress-strain behavior. DE and DF represent stress-relaxation and creep terminating in an equilibrium state. The dotted lines from G represent stress relaxation and creep terminating in a potential rupture mode.

The stress-strain curves represent the nonlinear viscoelastic response of an amorphous elastomer to an imposed strain, increasing directly proportionally to time.

In more recent work, Landel⁷ shows an interesting series of FKM elastomer stress-strain curves (Figure 4) plotted logarithmically. The curves, progressively displaced upward as the temperature is decreased,

are terminated at a point representing rupture. The family of curves represents a decreasing temperature run at one strain rate with the temperature normalized to Kelvin. By plotting an envelope around the rupture points, the curve in (Figure 3) is now emerging.

Failure envelope.-Smith's next approach was to run a non-reinforced FKM2 elastomer and plot the log of stress and strain at break, as shown in (Figure 5) (as opposed to the previous (Figure 4), which was plotted as the log of stress versus strain). The data points reflect 10 strain rates (from 0.02 to 20 inches per minute) for each of the nine temperatures noted. Again, the familiar parabolic curve is apparent. The data scatter in the low temperature area is understandable in light of the Tg curve (Figure 1) and the Meyer-Ferri curve (Figure 10). Both figures indicate that the rubbery characteristic is becoming "blurred" in this temperature range because microcrystallinity is appearing.

Filler reinforcement.-Table I points out the contribution of fillers to the source of strength of elastomers. At elevated temperatures, the contribution becomes greatly minimized⁸ as evidenced by Figures 6⁹ and 7¹⁰. The data, developed by Greensmith, Mullins, and Thomas¹¹ and plotted by Gent, represents critical fracture energy G_c , or critical strain energy release. The validity of a high temperature design model based on stress-strain properties for an unfilled, single-phase, non-crystallizable elastomer is more apparent after reviewing these figures. There is an obvious contribution by specific fillers at higher temperatures, but it is the contribution toward higher shear modulus rather than true stress at break.

Crosslink density.-Increasing crosslink density affects physical properties in the generalized manner described by Figure 8¹². Dependence of true stress at break for an FKM1C (highest molecular weight) elastomer with varying diamine curative levels is illustrated by Figure 9¹³. The diamines are not as efficient as the newer bisphenols. The physical contribution of chain entanglements is very apparent. The peak stress at break values are formulations that would be considered "undercured" by conventional compounding standards. Supplier data¹⁴ and other references^{15,16} give ample technical details of crosslinking chemistry. Our interest is primarily in the development of higher-modulus while optimizing other various critical physical properties such as tear strength and compression set.

Theory

Rubber elasticity.-"It is now well established that the stress in a deformed rubber originates within the chains of the network. Inter-chain interactions contribute negligibly to the stress ."¹⁷ (Figure 10) from Reference 18 illustrates the Meyer-Ferri experiment which helped to establish the importance of entropy as the deformation mechanism in rubber. The third law of thermodynamics is essentially satisfied by this experiment, illustrating that force is directly proportional to temperature using absolute (Kelvin) temperature as a base. Thermodynamics is thus firmly established as a contributing discipline for the understanding of other polymeric responses.

Intermolecular forces.-Intermolecular forces are the attractive forces between two molecules due to electrical imbalances. We are

considering the three major intermolecular force components which control physical strength, thermal properties, and solubility (compatibility).

Dispersion (London) forces. $-\delta_d$, are common to all matter. They are omni-directional and are a major contributor to the physical properties of materials. They are the only intermolecular force in non-polar materials. The individual attractive effect is relatively insignificant but cumulative with increasing molecular weight. Table II illustrates that a change in physical state from a gas, to a liquid, to a solid, is the direct result of dispersion forces.

Dipole (Keesom) forces. $-\delta_p$, also called orientation-electrostatic forces, are created when the vector sums of the various bond angles do not cancel, creating a net dipole. Methanol is an interesting model: two gases combine to create a liquid, (Figure 11). Dipole forces have a strong orientation effect often creating geometric species such as dimers, trimers, tetramers, and pseudopolymers. The model illustrated is complicated by a third intermolecular force, the hydrogen bond, Figure 12.

Charge transfer forces. $-\delta_h$, is a catch-all contribution (including hydrogen bonds) of a series of smaller intermolecular forces, all relatively directional like the dipole force. An interesting effect is illustrated in (Figure 13). CH_4 and CF_4 are symmetrical, non-polar molecules, the boiling points dictated by dispersion forces alone, and the difference due to different CH and CF binding energies. Fluorine substitutions of hydrogen raises the boiling point due to H-F interactions. The highest boiling point is for CH_2F_2 , illustrating the highly directional nature of the hydrogen bond.

Weight-Per Cent Fluorine

PTFE polymers.-PTFE (polytetrafluoroethylene) was the first totally fluorinated (perfluoro)/polymer (76 weight-% fluorine). PTFE represents the maximum chemical and thermal stability available in an aliphatic carbon backbone polymer. The "folded chain" molecular architecture, Figure 14¹⁹, precludes a rubbery phase because of the high per cent of microcrystallinity (50-70%).

FKM elastomers.-The rubbery analogs, FKM elastomers, are created by polymerization of two or more fluorinated monomers subsequently referred to as structural units such as vinylidene fluoride (VF₂), tetrafluoroethylene (PTFE), hexafluoropropylene (HFP), and perfluorovinylmethylether (PVME). The bulky side groups on the HFP (-CF₃) and PVME (-OCF₃) do not allow folded chain structures, and the random coil structure results. A Tg below room temperature, less than 30% microcrystallinity and a random coil structure are minimum requirements for elastomers as we know them.²⁰

Fluorine.-Weight-per cent fluorine in FKM elastomers ranges from 66% to 73.9%. Table III shows an estimated weight-per cent of both fluorine and hydrogen for the four generally utilized elastomers.

Hydrogen fluorine number ratio is also noted. Molecular weight differences (19 versus 1) understates the effect of hydrogen, which has a multiple role in FKM1-3 elastomers;

Hydrogen - Good effects

Cure site for dehydrohalogenation mechanism.

Improves low temperature flexibility.

Better physical properties at intermediate temperatures.

Hydrogen - Bad effects

Lowers thermal stability.

Attracts hydrogen bonding molecules (methanol, etc.).

Inherent site for acid-base interactions.

Temperature-Fluorine %.-Increasing weight-per cent fluorine raises the Tg because of molecular size and electronegativity differences, Table IV (hydrogen is strongly positive, fluorine strongly negative). Tg is the point of change in the slope of the curve of volume versus temperature, Figure 15²¹. It is generally accepted that all single phase, amorphous polymers have 0.025 (2^{1/2}%) free volume at Tg²². Comparison of physical properties of most amorphous, single-phase elastomers at equivalent temperatures corrected to Tg should give similar results. The WLF equation can be used to predict empirically, with surprising accuracy, property shifts up to 100°C above Tg.

Molecular Weight

Degree of polymerization.-Single-phase elastomers usually reach optimum processing properties at about 1000 structural units, Figure 16²³. Lower and higher degrees of polymerization (molecular weight) are often available, with a range of 500 to 2500 units not uncommon. Some typical estimated degrees of polymerization are listed in Table V. A plot, Figure 17, of four FKMI polymers having increasing Mooney viscosity

(molecular weight) shows improvements in tensile, elongation, and compression set. M100 modulus and durometer are relatively unchanged.

Compression set improves with increasing degree of polymerization because of chain entanglements.

Physical entanglements.-Additional entanglements are created by crosslinking, Figure 18²⁵. Kramer and Ferry²⁶ note that a typical EPM (56 mole % ethylene) has a physical entanglement every 50 structural units. Polystyrene has a physical entanglement every 175 structural units. FKM1 polymers might have a physical entanglement every 150 structural units, and FFKM, every 175 structural units (due to higher bulky fluorine ratios).

The concept of physical entanglements does not lend itself to classical solutions. High molecular weight crosslinked polymers have properties that normally would be predicted by a crosslink density twice as high as the known value.

Molecular weight effects.-The effect of increasing molecular weight on tensile strength is apparent at higher temperatures. Noted later is the effect on gas-liquid-elastomer interactions resulting in improved resistance to blistering and fracture.

Gas-Liquid-Elastomer Interactions

Failure modes.-The failure modes of rubber components through sponging, blistering, and rupturing are logically caused by diffusion of gases into the elastomer. The idea of diffusion is intuitive and is readily acceptable, in view of all elastomers having $2^{1/2}\%$ void area at Tg, noted earlier. Van Amerongen's classic work on diffusion²⁷ points out that the diffusion coefficient is dependent on molecular

construction, pressure, solubility and Tg. Simplistically, we will define gas-liquid-elastomer interactions by stating: DIFFUSION creates the problem, and SOLUBILITY exaggerates the problem.

Diffusion.-Diffusion²⁸ is the net transport of material within a single phase in the absence of mixing. Experiment and theory have shown that diffusion can result from pressure gradients (pressure diffusion), temperature gradients (thermal diffusion), external force fields (forced diffusion), and concentration gradient diffusion.

Solubility.-Potential solubility of the CO₂ and H₂S gases in elastomers was reviewed by the solubility parameter concept.

Solubility parameter concept.-Data for solubility parameters, δ , was developed on the basis of the Hildebrand^{29,30} regular solution theory, using the Hansen³¹ modification. This modification considers δ to be the sum of three component forces: $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$ where

δ_d = dispersion (London) - common to all matter,

δ_p = dipole (Keesom) forces - created by permanent dipoles, and

δ_h = charge transfer forces (including hydrogen bonds).

Hildebrand states that a difference of four or less δ units $\{(J/m^3)^{1/2} \cdot 10^{-3}\}$ between solvent and solute indicates a potential solubility interaction. Solubility parameter data for Table VI and Table VII were derived by using the molecular additive constants technique as advanced by Fedors³² from unpublished data by Beerbower³³.

CO₂ solubility.-CO₂ with $\delta=15.1$ has a theoretical compatibility mix with FKM1 through FFKM-4, appearing more soluble with increasing weight-per cent fluorine. In terms of molecular thermodynamics, it has a doubly degenerate bending mode³⁴ (meaning that it vibrates both perpendicular

and parallel to a plane surface), which makes it a very mobile molecule.

H₂S solubility.-H₂S with $\delta=22.6$ also shows theoretical compatibility decreasing with increasing weight-per cent fluorine. Previous testing by Seals Eastern had indicated that increasing weight-per cent FKM elastomers equivalently compounded were less resistant to sour crude blistering.

Conclusion

The contradictory results on H₂S (theoretical solubility versus actual data) lead us to believe we had both a physical problem of diffusion and a thermodynamic conflict.

Physical problem-layers.-There is relative agreement that a solvent-solute diffusion mechanism for liquids is one or more diffusion fluxes created as gas-liquid transports into the elastomer. This phase phenomenon is described variously as:

"Plane of no net molal flow" for binary mixtures²⁸ ,
the thermodynamic concept of a hypothetical fixed
reference plane, Figure 20,

"Integral surface layer concept of sublayers"³⁵ due to
solvent-solute interaction (Ueberreiter-1968),

"Membrane osmometry concept"³⁶ whereby elastomer serves as
both membrane (surface) and solute (body).

In all cases, the equilibrium gas-liquid combination diffuses into the solute (elastomer) until equilibrium is again attained. A change in equilibrium causes a reverse flow, rate dependent on solubility. The boundary layer, the weak member, is dependent on molecular weight for physical strength through chain entanglements.

Failure Mechanisms

Critical flaw sites³⁷. - Natural flaws, 40 μm or less, inevitably occur in elastomers. Tear propagates from these sites when a large enough stress is applied. Many compounding ingredients (Ex.-litharge-a typical FKM acid acceptor) have particle sizes in this range so potential fracture preconditions are well established.

Table VIII³⁸ is a comprehensive cross reference offering a perspective of size relationships between elastomers, fillers, and other ingredients.

Assuming a natural flaw site, Figure 19³⁹, is occupied by diffused gas, an equilibrium change creates a positive internal pressure. At a critical pressure (P_c), the result is a probable blister or rupture mode occurrence.

Blistering.- Blistering, usually associated with a highly elastic solid, results when the following conditions are met:

- a. gas supersaturated,
- b. durometer-low (low shear modulus),
- c. crosslink density-low,
- d. elongation-high (>200%).

"Equation(1)" appears to adequately describe this occurrence (E=Young's modulus).

$$P_c = 5E/6 \quad (1)$$

Fracture.-Fracture (rupture) is the failure mode of a linear elastic solid. Gent suggests this mechanism occurs when the following preconditions exist:

- a. durometer-high (high shear modulus),
- b. crosslink density-high,
- c. elongation-low (<100%)

"Equation(2)" is suggested by Gent to numerically define this mode of fracture.

$$P_c = 4/3 \lambda_b \sigma_b \quad (2)$$

Log $\lambda_b \sigma_b$ (true stress at break) values are available from Figure 9. The rupture failure mode is typical of high modulus seals. The surface "flaking" or lenticular failure probably occurs with an equilibrium shift before steady state diffusion occurs. The deeper internal fissuring, normally parallel to the diffusion plane, is assumed to initiate at a natural flaw site near the "plane of no net molal flow", (Figure 20⁴⁰), during an equilibrium shift. The failure proceeds as a high speed propagation mechanism⁴¹ until there is sufficient internal energy dissipation to arrest the crack growth.

CONCLUSIONS

Diffusion of gas into elastomers is assumed unavoidable due to physical and thermodynamic interactions. On decompression, the blistering or rupturing is initiated at naturally occurring flaw sites. Resistance to blistering is a function of pressure, flaw size, and elastomer shear modulus. Shear modulus is the only variable we have control over. Figure 21, developed by Gent⁴², is an excellent story describing graphically the interactions of the three variables. To vary shear modulus, the technologist can vary crosslink density and filler type. Increasing molecular weight is predicted to increase fracture energy⁴³ and has been verified by functional and field testing.

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⁴¹Reference 8, p. 435.

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⁴³Reference 8, p. 428.

NOMENCLATURE

C	Celsius temperature
E	Young's modulus
E_b	elongation at break
G	shear modulus
G_c	critical fracture energy (critical strain energy)
K	Kelvin temperature
P_c	critical pressure (elastic instability)
r_o	radius-original (internal flaw or crack tip)
RR'	plane of no net molal flow
T_g	glass transition temperature
T	temperature
V	volume
δ	solubility parameter
δ_d	dispersion force parameter
δ_h	hydrogen bond forces, parameter
δ_p	orientation-electrostatic (dipole) parameter
ϵ	strain, elongation %/100
ϵ_b	strain at break
λ	Extension ratio (length of the stretched specimen per unit initial length)
λ_b	Extension ratio at break
σ	stress (load per unit initial area)
σ_b	stress at break

ABBREVIATIONS

FKM	hydrofluorocarbon elastomer (D1418)
FFKM	perfluoroelastomer (D1418 prop.)
FKM1	low fluorine content
2	medium fluorine content
3	high fluorine content
FKM1A	low viscosity (molecular weight)
B	medium viscosity
C	high viscosity

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TABLE I

Strength of Elastomers

Elastomer type	Source of strength
Single-phase non-crystallizable	Viscoelastic processes Molecular network Orientation of chains
Filled, non-crystallizable	Increased energy dissipation Deflection and bifurcation of microcracks Cavitation
Crystallizable	Formation and deformation of crystalline domains
Block copolymers	Plastic domains

TABLE II

Building Molecular Weight**By Adding CH₂ Groups**

<i>Chemical Formula</i>	<i>Common Name</i>	<i>Molecular Weight</i>	<i>Physical State</i>
CH ₄	Methane	16	Gas
C ₂ H ₆	Ethane	30	Gas
C ₃ H ₈	Propane	44	Gas
C ₄ H ₁₀	Butane	58	Gas
C ₅ H ₁₂	Pentane	74	Liquid
C ₁₇ H ₃₆	Kerosene	240	Liquid
C ₁₈ H ₃₈	Paraffin	254	Solid-soft
C ₅₀ H ₁₀₂	Hard Waxes	702	Solid-brittle
C ₁₀₀ H ₂₀₂	LMW Polyethylene	1402	Solid-tough

TABLE III

FKM Elastomers - Wt. % Fluorine

	<u>Wt %- F</u>	<u>Wt %- H</u>	<u>Molal %- H/F</u>
FKM 1	66.0	1.86	53.5
FKM 2	68.5	1.40	38.9
FKM 3a	69.4	1.24	34.0
3b	70.0	1.14	31.0
FFKM 4	73.9	0.0	0.0

TABLE IV

Glass Transition (T_g) vs. Fluorine Wt.-%

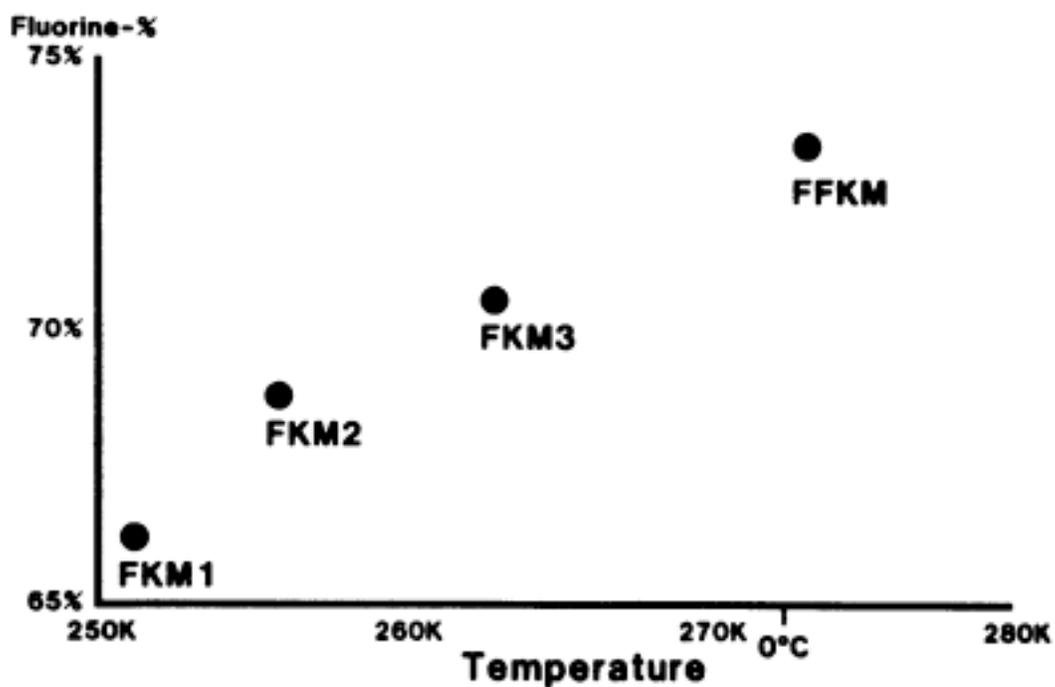


TABLE V

Degree of PolymerizationFKM - Structural Repeat Units*

	<u>FKM 1</u>	<u>FKM2</u>	<u>FKM3</u>	<u>FFKM</u>
<u>Mooney Value:</u>				
a Low	750	900		
b Medium	1100	1250	950	400-800
c High	2200			

* estimated

TABLE VI

FKM Solubility Parameters^{1,2}

	<u>1</u>	<u>2</u>	<u>a</u>	³ <u>b</u>	<u>4</u>
δ_d	15.4	14.3	14.7	13.5	12.1
δ_p	6.8	5.1	5.7	4.7	2.9
δ_h	9.2	7.2	8.2	8.8	3.5
δ	19.1	18.8	17.8	15.7	12.9

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$$

- based on Group Contributions (unpublished)
 - Beerbower 3/18/80
- CGS Conversion (+) 2.046

TABLE VII

Gas Solubility Parameters

	<u>CO₂</u>	<u>H₂S</u>	<u>CH₄</u>	<u>N₂</u>	<u>He</u>
δ_d	11.1	19.4	9.2	8.1	3.3
δ_p	7.2	8.2	0	0	0
δ_h	7.2	8.2	0	0	0
δ	15.1	22.8	9.2	5.1	3.3

1. A. Beerbower 3/29/80

2. STP - 25°C

3. CGS Conversion (+) 2.048

TABLE IX

Failure Modes - Equations - Preconditions

<i>Failure Mode</i>	<i>Failure Equation</i>	<i>Elastomer Preconditions</i>
Blistering	$PC - 5E/6$	Lower durometer, lightly crosslinked elongation > 200% highly elastic gas supersaturated
Lenticular (rupture)	$P_c = 4/3 \sigma_b \lambda_b$	High durometer, tightly crosslinked elongation < 100x, linearly elastic

1. A. Gent, Conversation 3/31 /80

FIG. 1

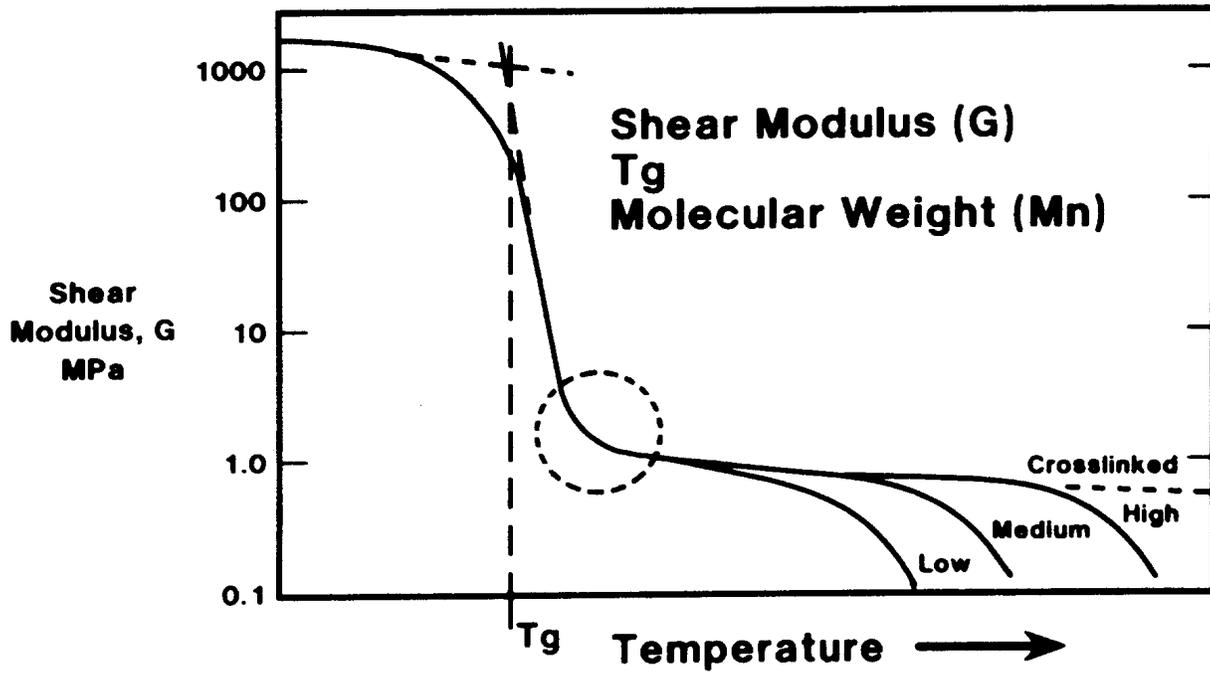


FIG. 2

**MODULUS VS. TEMPERATURE
FKM 1**

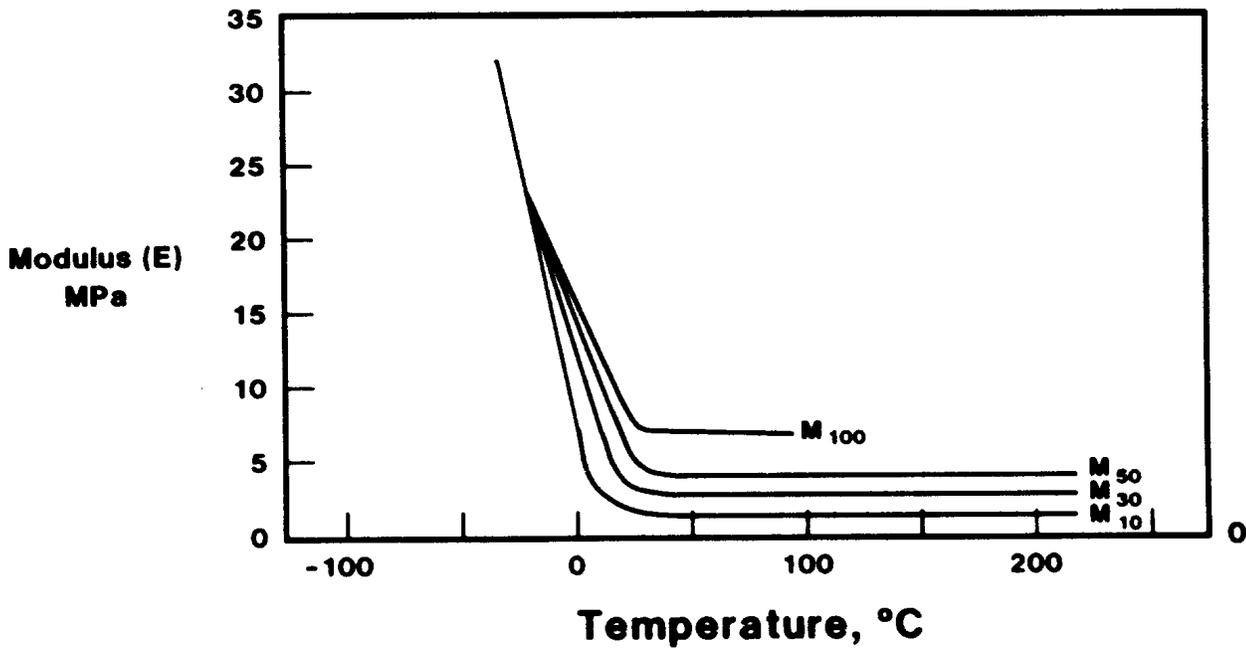
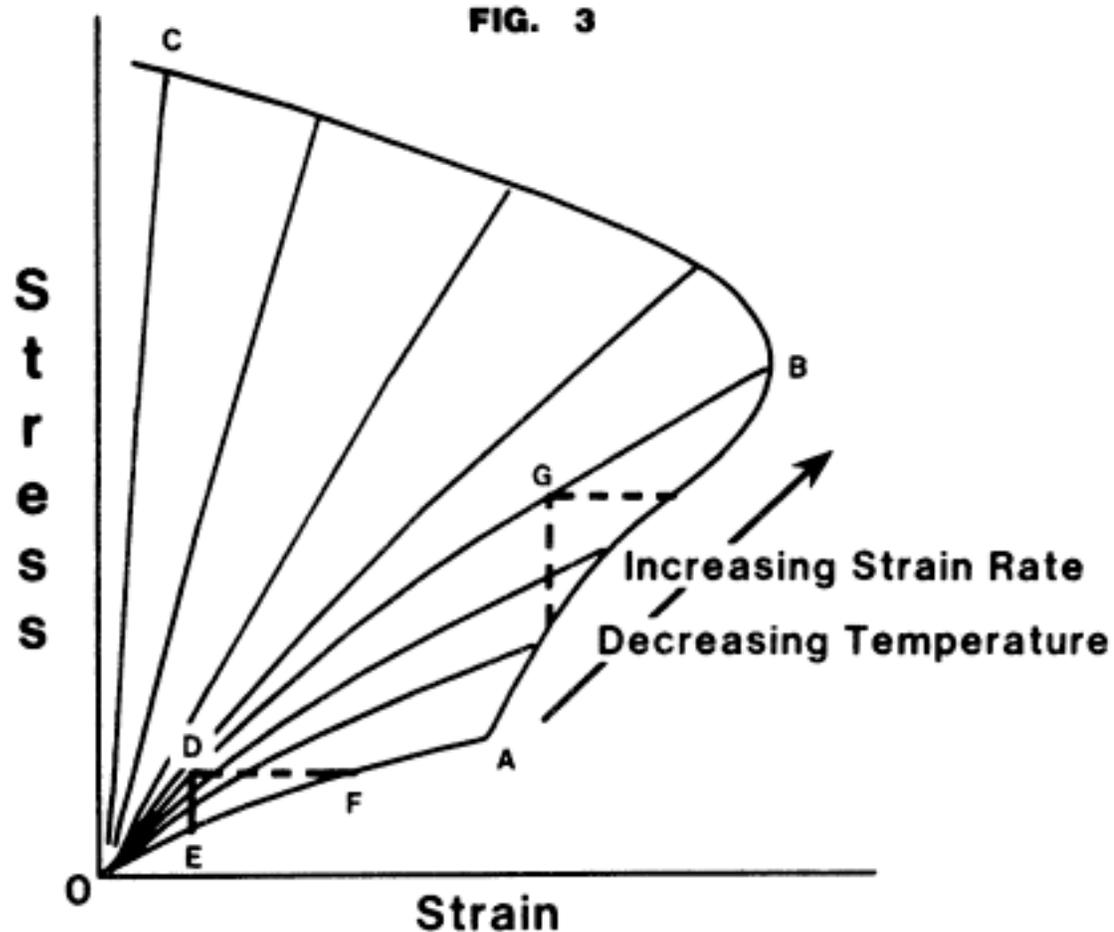


FIG. 3**FIG. 4**

Stress-Strain Curves, Plotted Logarithmically, For a Fluoroelastomer

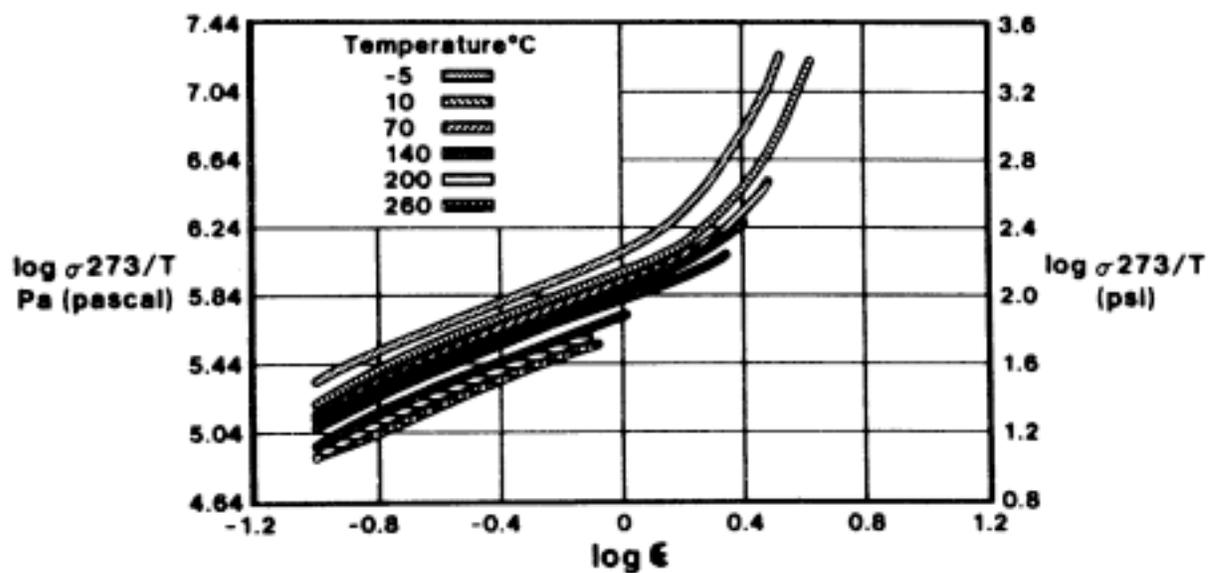


FIG. 5

Fluoroelastomer Failure Envelope

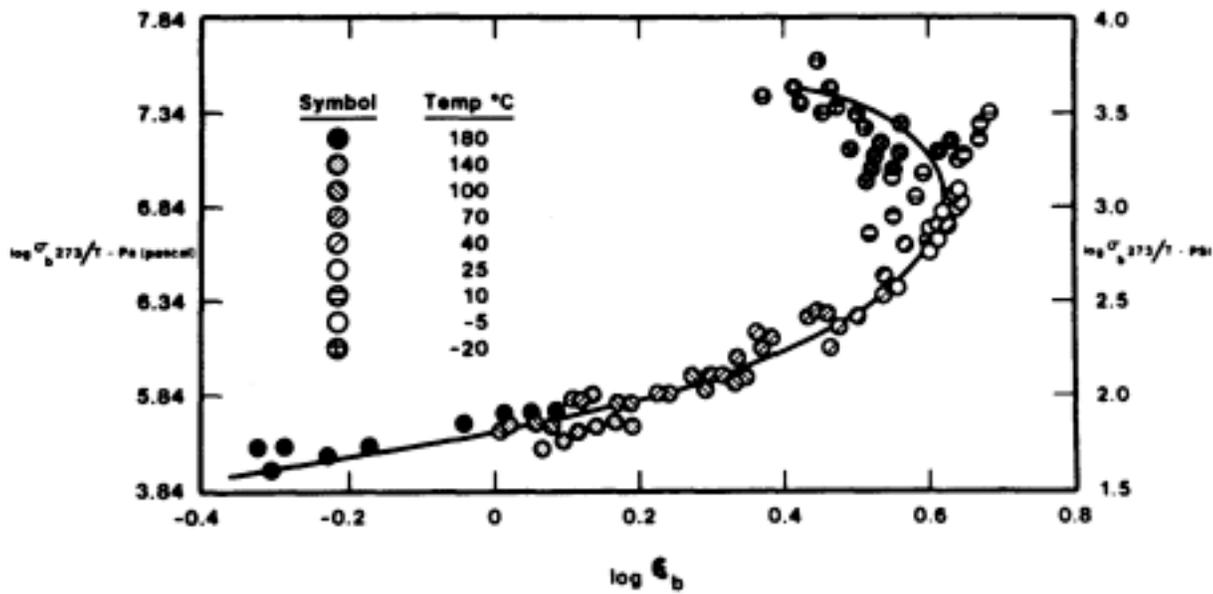


FIG. 6

Fracture Energy-G Amorphous Elastomer-Nonreinforced

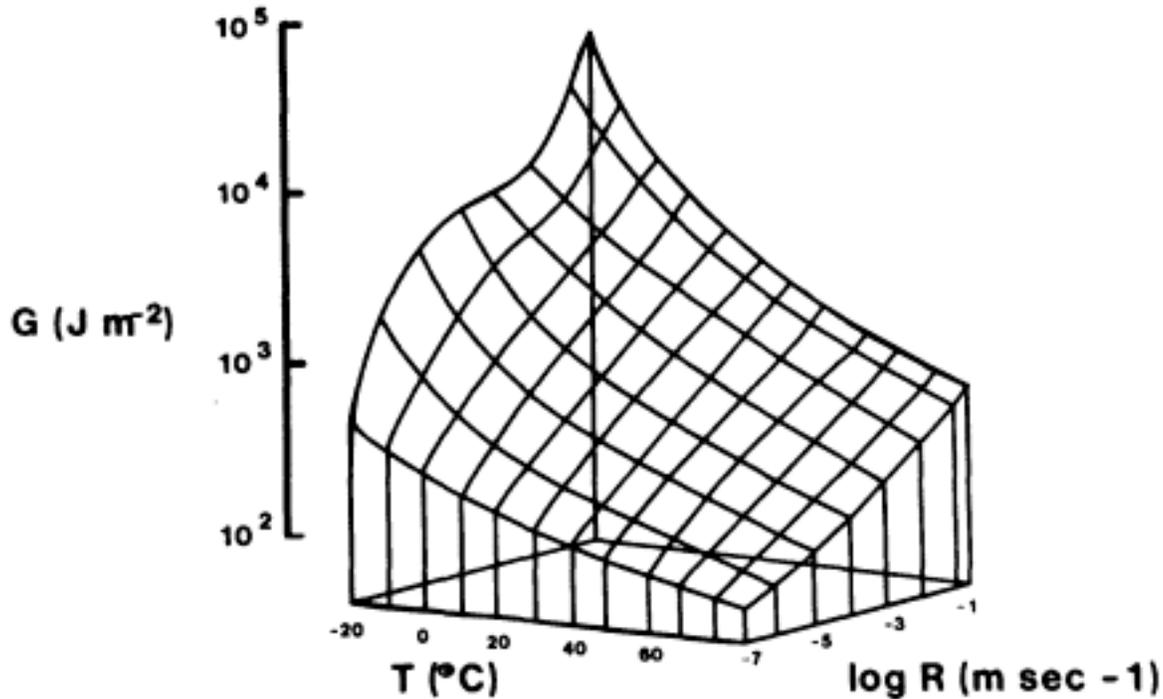
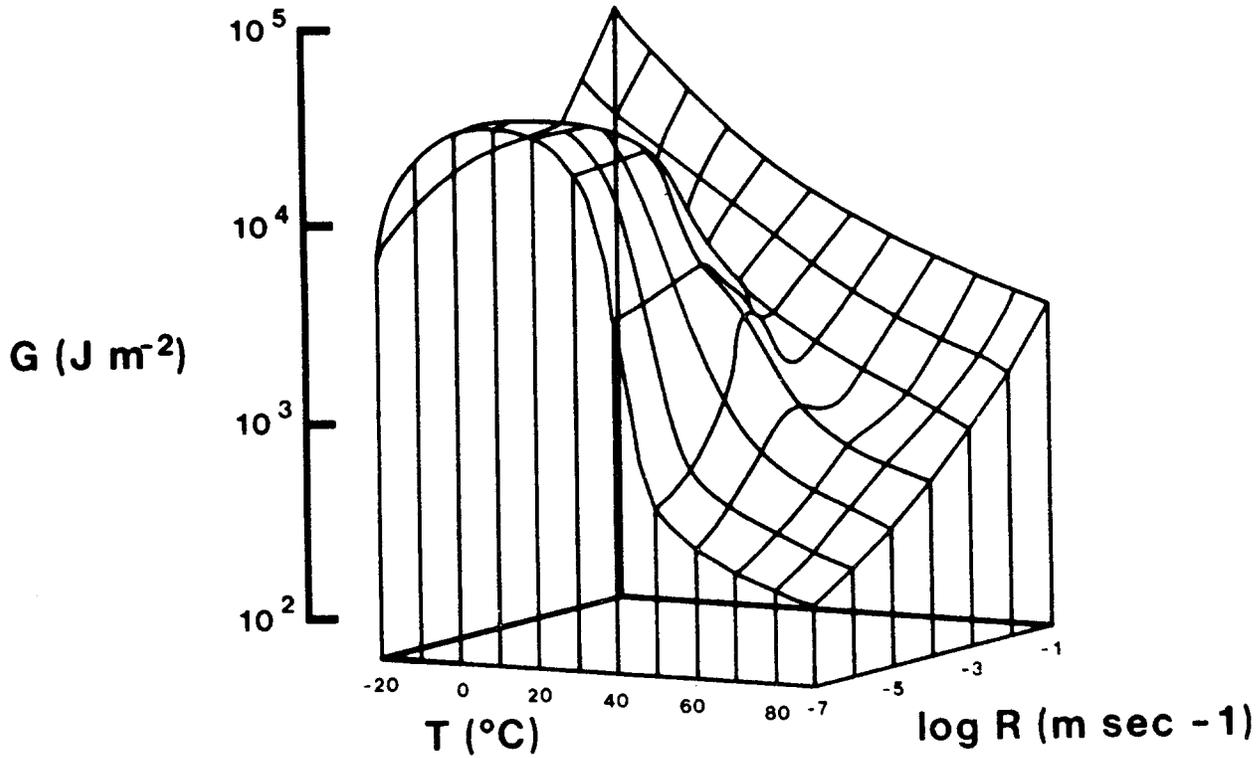


FIG. 7

Fracture Energy-G Amorphous Elastomer-Reinforced



VULCANIZATE PROPERTIES

FIG. 8

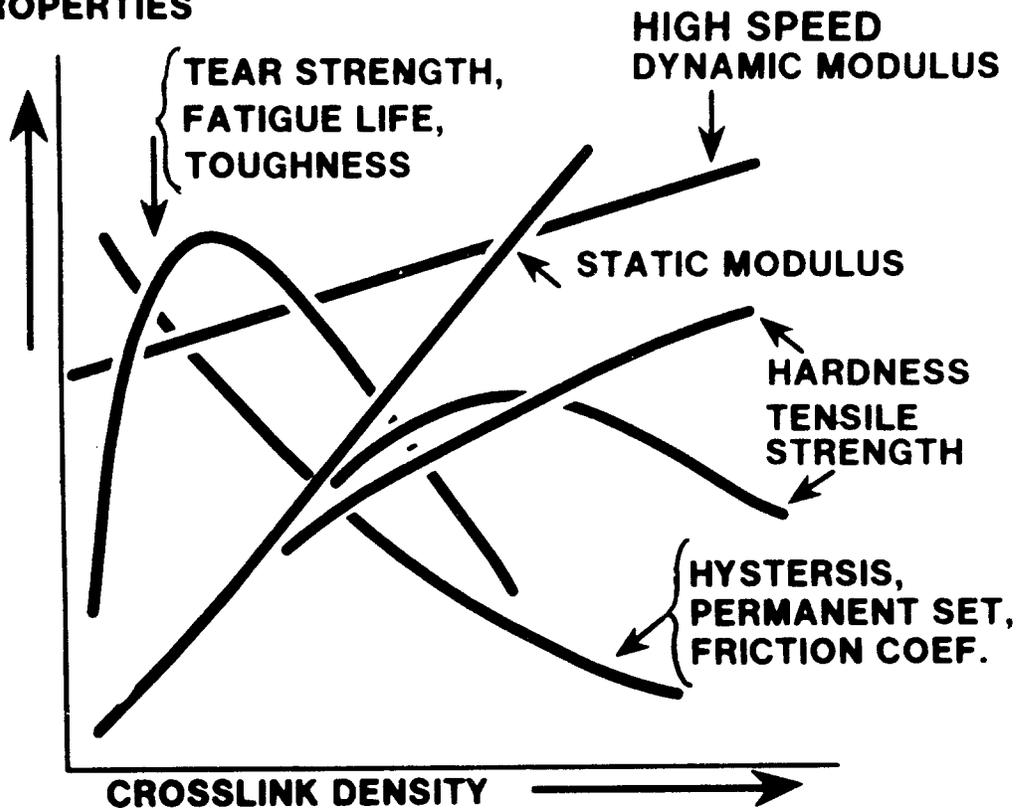


FIG. 9

Curative Level Response FKM 1C

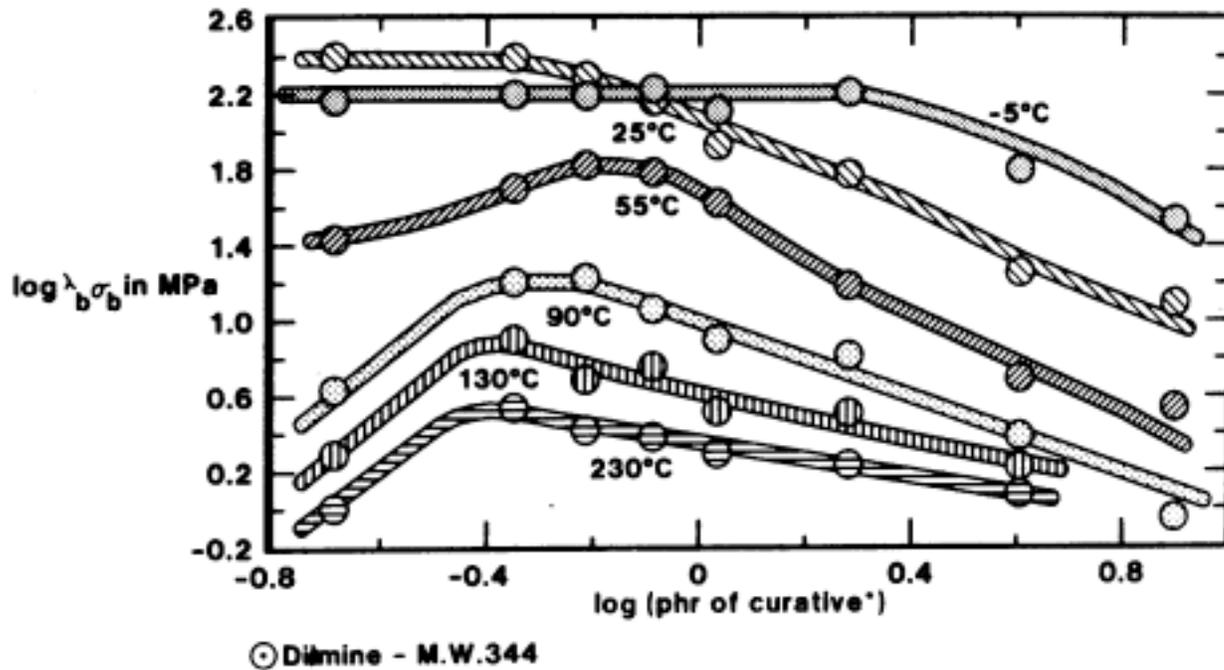


FIG. 10

Stress vs. Temperature at Fixed Length

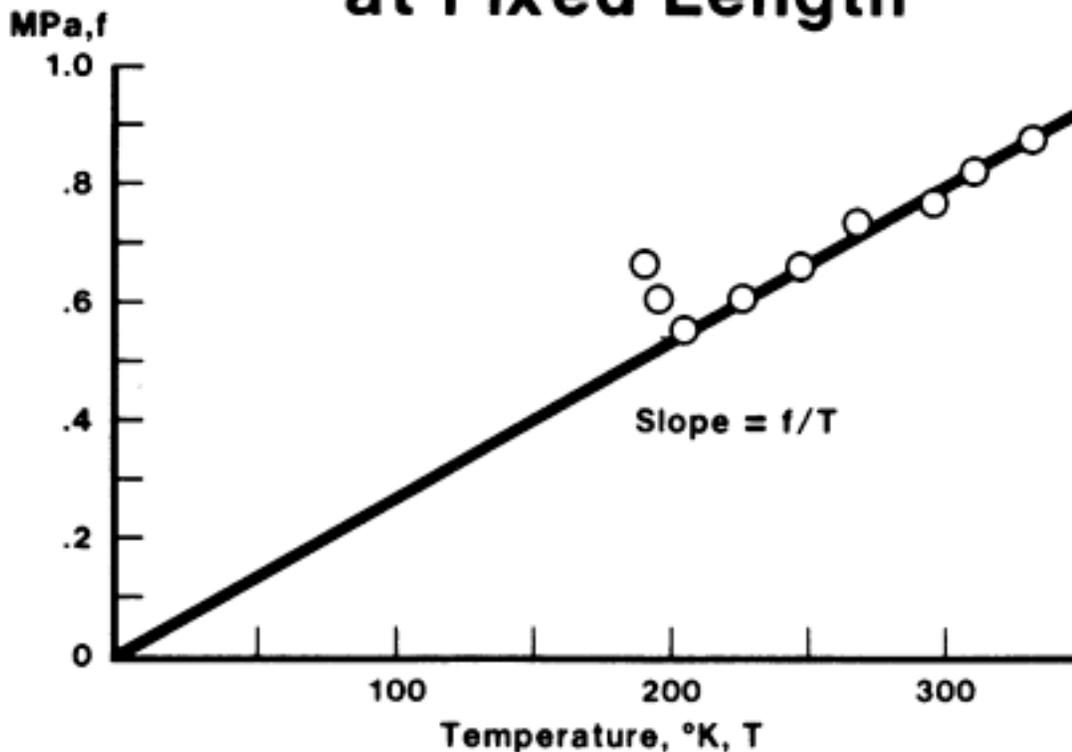


FIG. 11

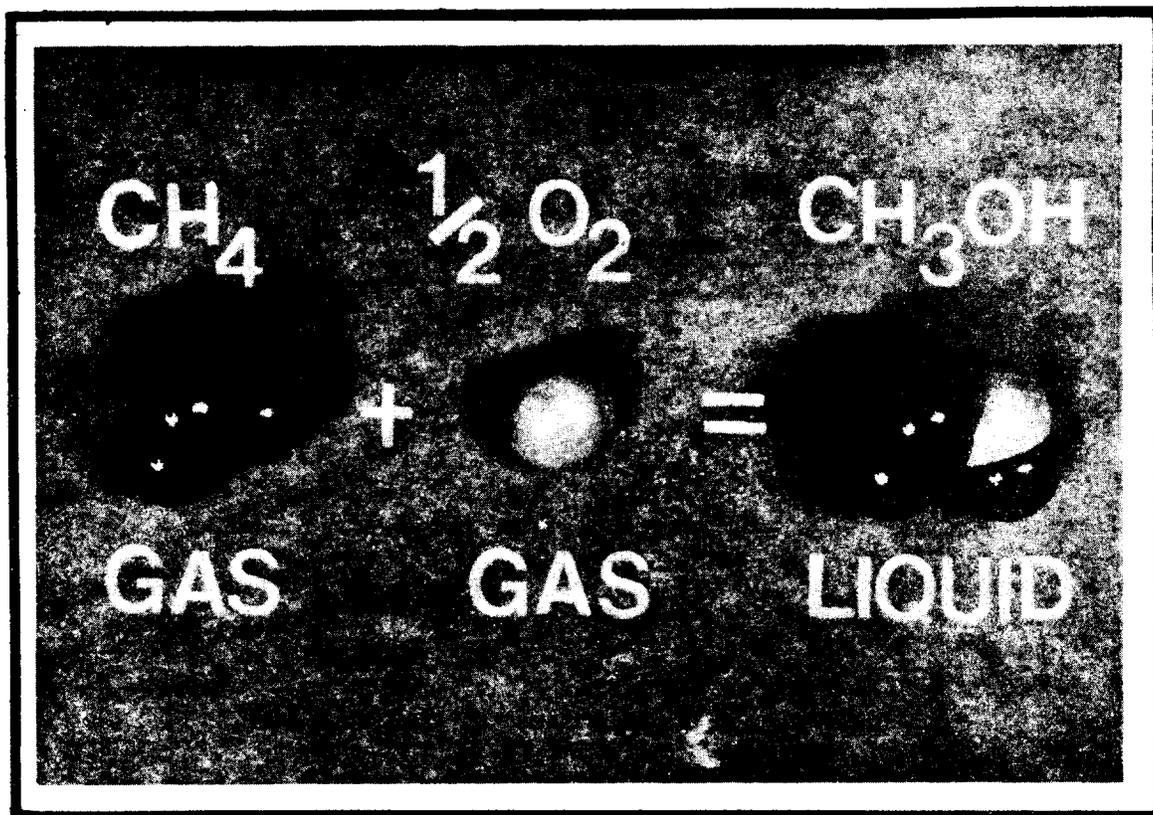


FIG. 12

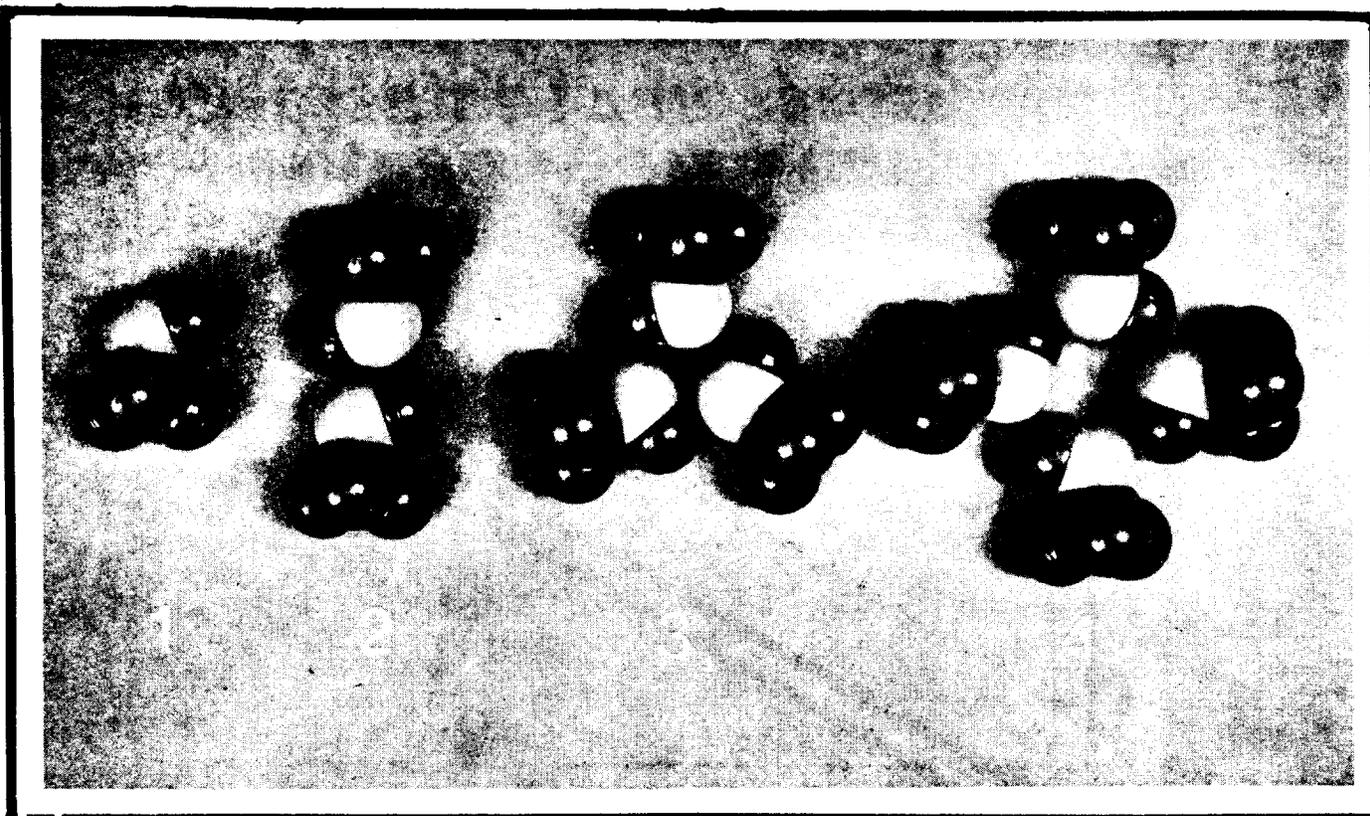


FIG. 13

CH₄ - CF₄ Derivatives - Boiling Points

Temperature °C

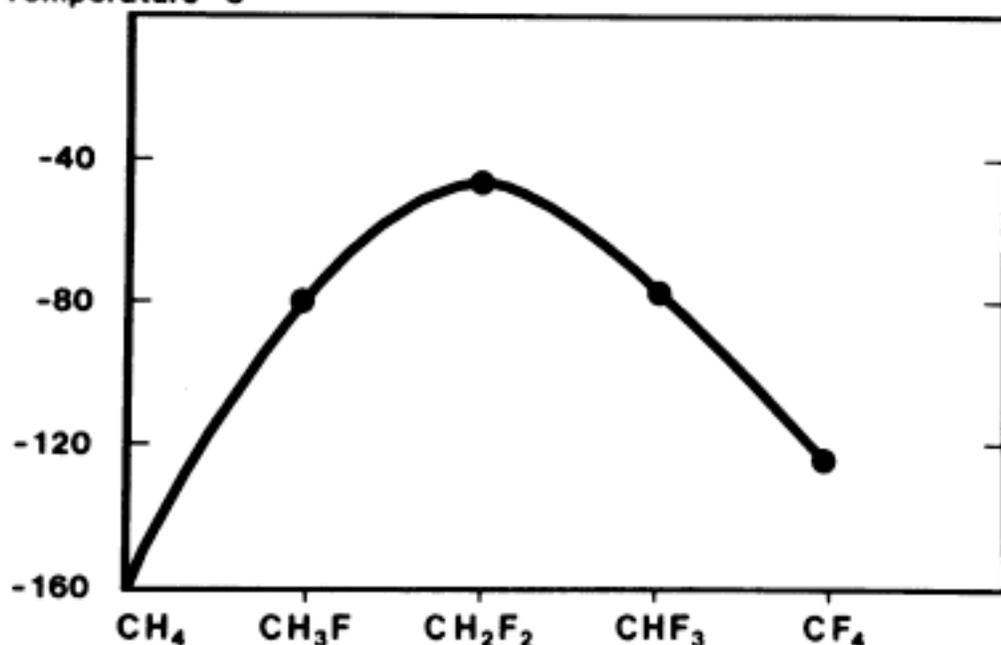
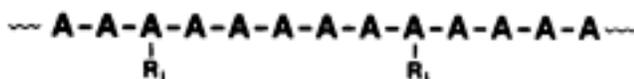


FIG. 14

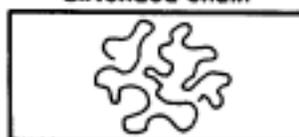
POLYMERIC STRUCTURES

PRIMARY

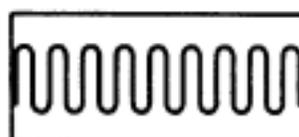


Extended chain

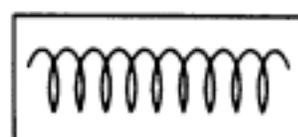
SECONDARY



Random coil



Folded chain



Spiraled chain (helix)

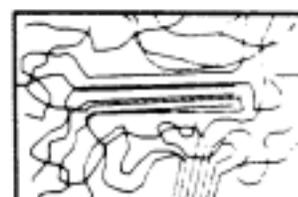
TERTIARY



Cell-structure of random coils



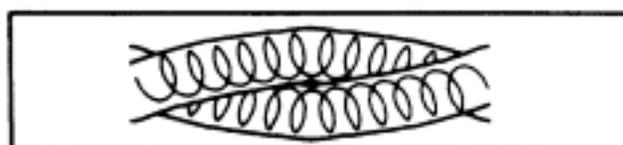
Spaghetti-structure



Fringed micelle



Polymer crystal with folded chains



Over-spiraling (super-helix)

FIG. 15

Amorphous & Crystalline Polymers

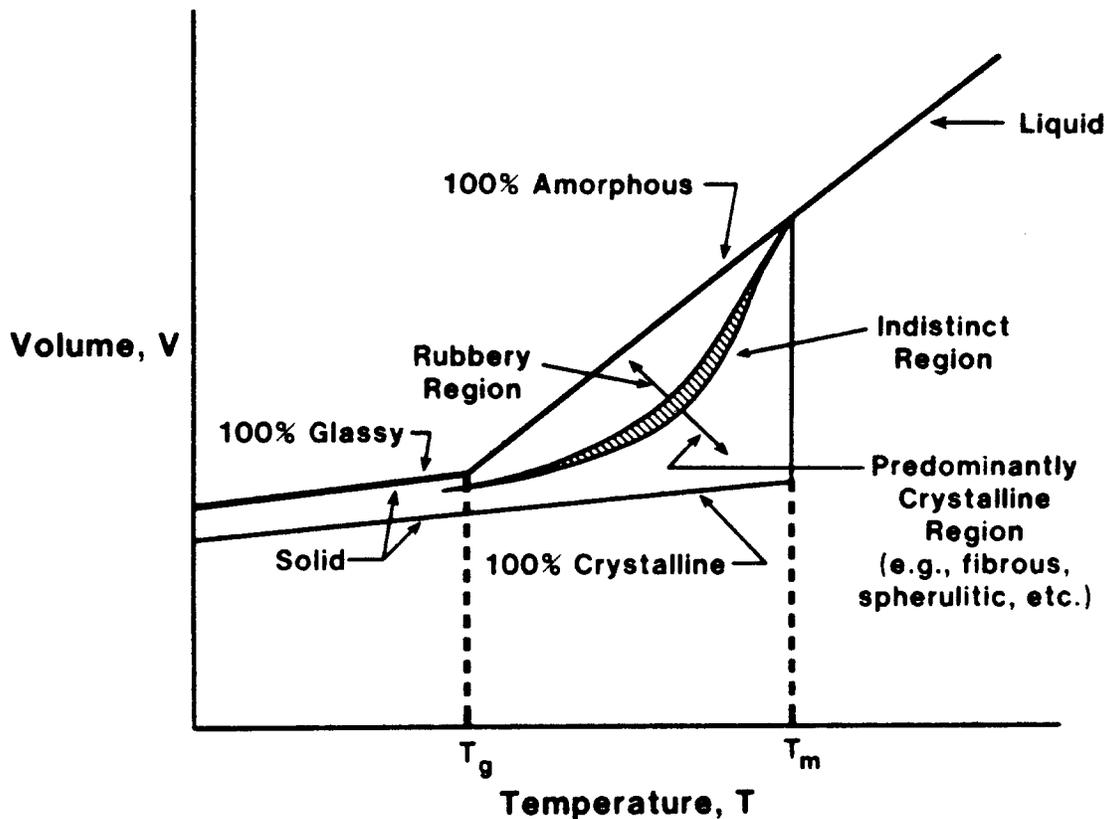


FIG. 16

Tensile Strength vs. Degree of Polymerization

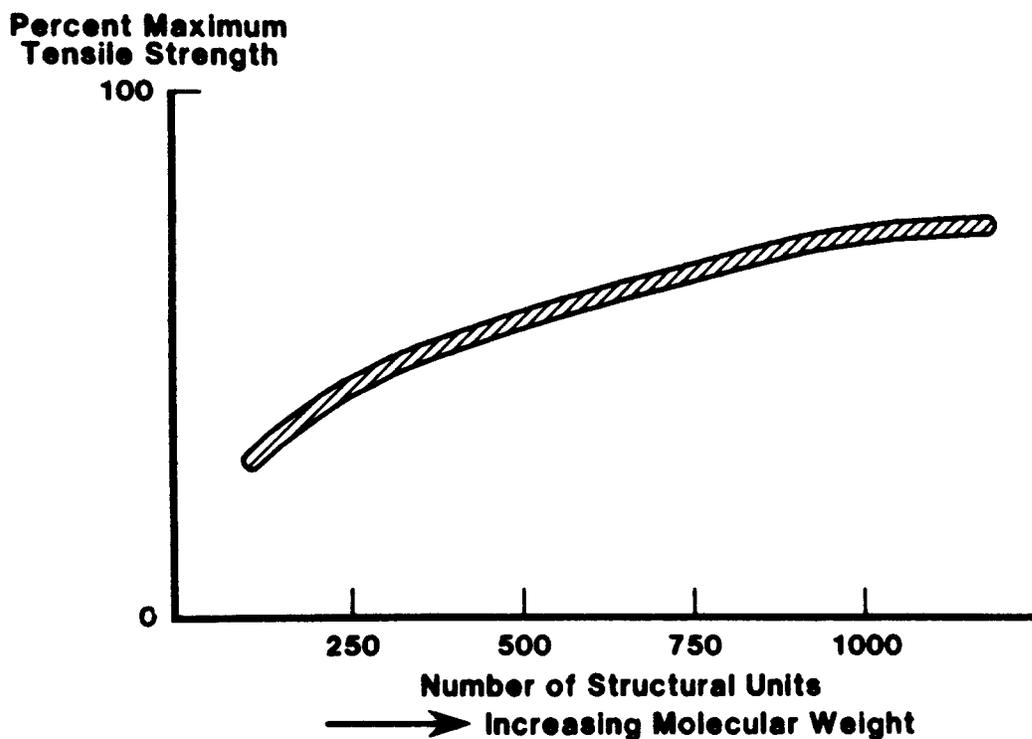


FIG. 17

Molecular Weight - Physical Properties

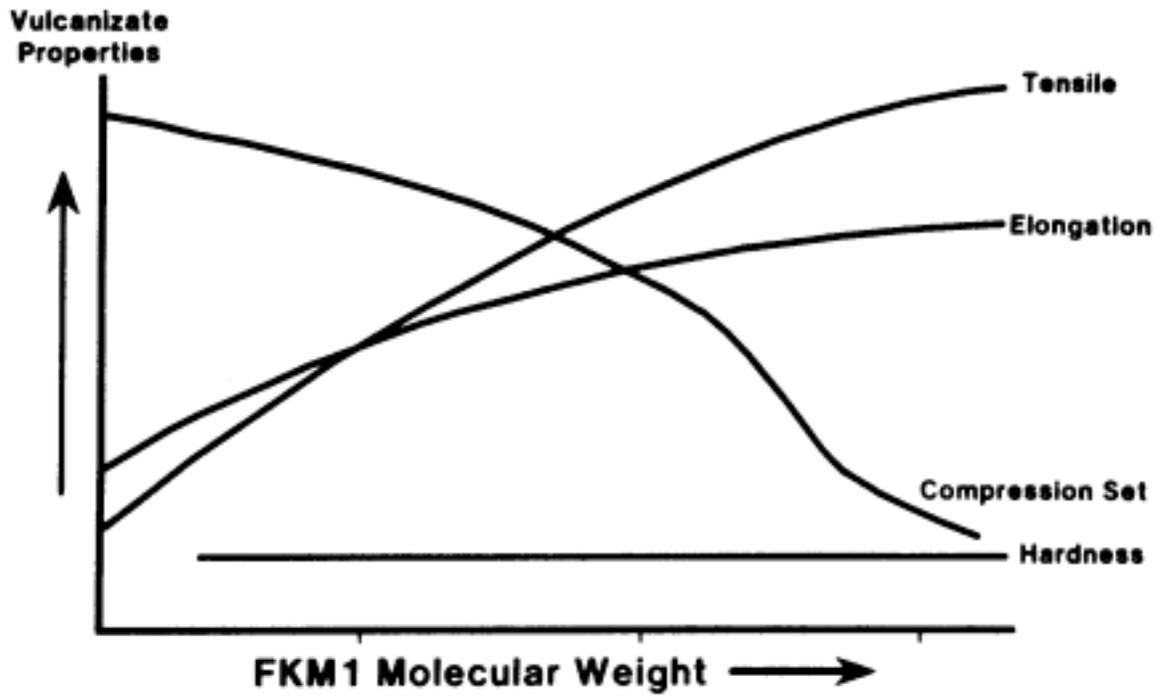
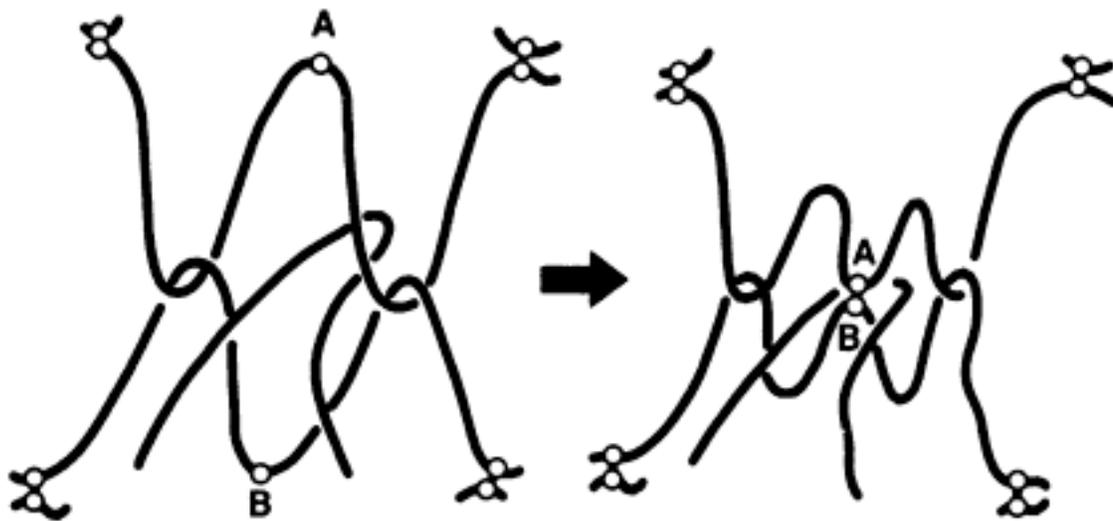


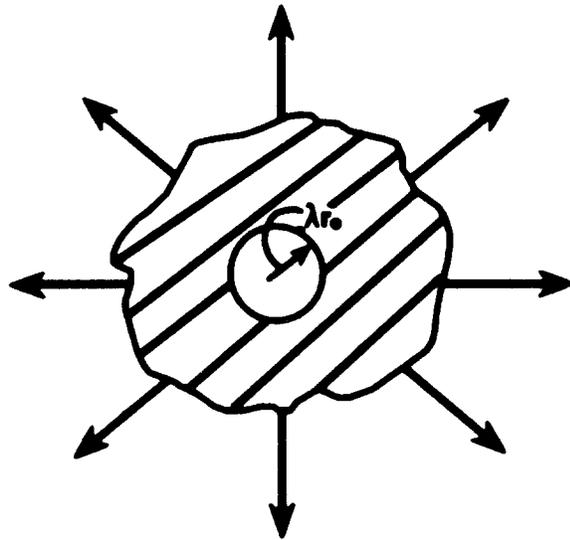
FIG. 18



Generation of effective entanglements during crosslinking.

FIG. 19

Cavity Expansion - Triaxial Tension

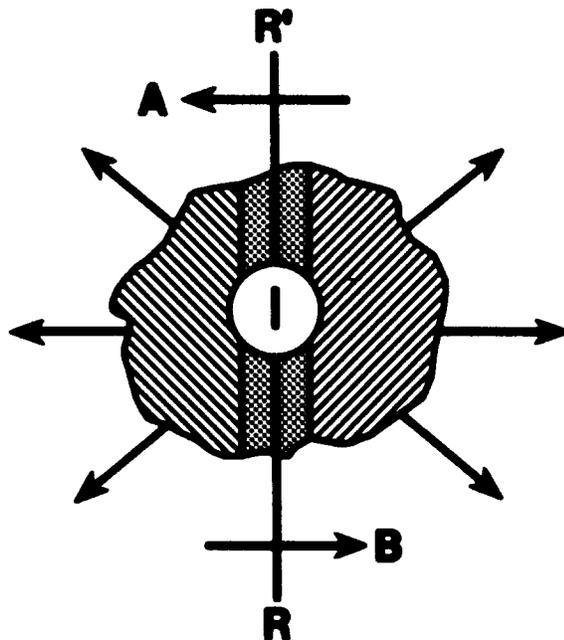


$$r_0 < 1/\mu m$$

λ = expansion ratio

FIG. 20

Diffusion Fluxes



RR' = Plane of NO NET MOLAL FLOW

FIG. 21

Critical Pressure - Cavity Size - Shear Modulus Relationships

